The Malaysian Journal of Analytical Sciences, Vol 14 No 1 (2010): 24 - 31

EFFECTS OF INDUCED SALINITY ON BOD_5 REACTION KINETICS OF RIVER WATER SAMPLES

(Kesan Peningkatan Kemasinan Terhadap Kinetik Tindak Balas Keperluan Oksigen Biokimia 5 Hari Menggunakan Sampel Air Sungai)

Zaki Zainudin[1*], Maketab Mohamed[2], Mohd. Rosslim Ramli[3]

[1]*Water Resources Technical Division, Institution of Engineers Malaysia, 46720 Petaling Jaya, Selangor Darul Ehsan*
[2]*Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia*
[3]*Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia*

**Corresponding author: zakizainudin@gmail.com*

Abstract

Biochemical Oxygen Demand (BOD) is a typical parameter used in assessing organic pollution strength in surface waters and is normally tested over a 5-day period at an incubation temperature of 20°C (BOD_5). The accuracy of this constituent, in assessing organic contamination under brackish conditions has always been known to be somewhat limited as elevated concentrations of chloride (Cl^-) disrupts microbial activity from osmotic cellular degradation, causing the bottle decay rate, k_1, to be effected. The aim of this study was to quantify the effects of induced salinity on k_1, with varying levels of sodium chloride (NaCl) concentration (5 – 25 ppt), towards six mildly polluted to polluted tropical river water samples. The observed variations ranged between 0.10 – 0.25/day of k_1 for the stipulated samples using the Thomas graphical method for determination of the k_1 rate constant. Sg. Rawang depicted the highest quantum of difference in k_1, with decrement from 0.754/day (0 ppt) to 0.513/day (25 ppt), whereas Sg. Klang showed the lowest quantum, from 0.306/day (0 ppt) to 0.265/day (25 ppt).

Keywords : BOD_5 saline, brackish, estuarine, bottle decay rate

Abstrak

Keperluan Oksigen Biokimia (BOD) adalah metodologi biasa yang digunakan untuk menilai kekuatan pencemaran bahan organik dalam air dan biasanya diuji dalam jangka masa 5 hari pada suhu inkubasi 20°C (BOD_5). Ketepatan BOD_5, untuk menilai kontaminasi organik dalam air masin sememangnya diketahui agak terhad akibat daripada kandungan klorida (Cl^-) tinggi yang mengganggu aktiviti mikrob, di mana berlakunya pelupusan sel dari proses osmosis, yang seterusnya menyebabkan gangguan terhadap kadar pereputan dalam botol (k_1). Tujuan kajian ini adalah untuk menghisab kesan kemasinan terhadap k_1, dengan meningkatkan kepekatan Natrium Klorida (NaCl) secara berperingkat, antara 5 – 25 bpj, terhadap enam sampel air sungai yang diklasifikasikan sebagai sedikit tercemar hingga tercemar. Didapati variasi k_1 umumnya berada antara 0.10 – 0.25/sehari menggunakan metodologi pengukuran grafikal Thomas. Sg. Rawang menunjukkan perbezaan ketara dalam nilai k_1, dengan kejatuhan daripada 0.754/sehari (0 bpj) ke 0.513/sehari (25 bpj), manakala Sg. Klang pula menunjukkan perbezaan paling minima dari 0.306/sehari (0 bpj) ke 0.265/sehari (25 bpj).

Katakunci : BOD_5 air masin, pencemaran organik di kawasan kuala sungai, kadar pereputan dalam botol

Introduction

Biochemical Oxygen Demand (BOD) is a fundamental parameter used in the assessment of organic contaminants present in water and wastewater. The parameter was first used in the early 1900s as an indicator of organic contamination from sewage sources in the United Kingdom (UK). An incubation time of 5 days at 20°C for testing, brought about the acronym BOD_5, with the primary justification that the maximum retention time of organic pollutants from sewerage sources of rivers in the UK was in accordance to these conditions [1]. The test itself in-turn, is primarily governed by three things; (1) the amount of biodegradable organic matter present, (2) mix culture of microbial population that propagates the degradation and (3) acceptable dissolved oxygen levels for microbial aerobic respiration. The amount of biodegradable organic matter present (left hand side of the Eq. 1.1), is the primary constituent of concern measured in the test, as excess amounts of organic matter may contribute towards in-stream oxygen depletion, commonly referred to as the DO sag [2] ;

$$C_nH_aO_bN_c + (n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c)O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right)H_2O + cNH_3 + NewCells \quad (1)$$

A universal qualifier used in BOD testing is that, only the carbonaceous fraction (or cBOD), is measured as this portion truly reflects the biodegradable organics present. The resulting ammonia, NH_3-N, which is a product of the degradation, exhibits its own oxygen demand after a few days, during the transformation of NH_3-N to NO_2-N and NO_3-N (nitrification). This oxygen demand is referred to as nitrogenous BOD or nBOD. In order to inhibit the effects of nBOD, nitrification inhibitors such as TCMP (2-chloro-6-(trichloro-methyl) pyridine) is utilized [3]. Throughout the degradation process, there must be sufficient levels of dissolved oxygen (DO) in the BOD test bottle, preferably above 2 mg/l. Depletion of DO below this value at any time during the test, will incur anoxic conditions, causing stress to the microbial population, hence affecting the BOD readings. If the value falls below 2 mg/l on the fifth day, the sample will simply be rejected and not considered to be part of the result. This is why many analytical references on BOD testing often recommend preparation of serial dilutions of the same sample, where incubation is done simultaneously [1].

The final variable for consideration is the quantity and type of microorganisms present. The microorganisms, which drive the degradation process can either be introduced through seeding or assumed to be already present in ambient water sample. As an added precautionary measure, seeding is often recommended by analytical references [3]. Though being the case, the quantification of the microbial population in the BOD tests remains arbitrary in many practices. This does not mean that this variable is unimportant; after all it is the microorganisms that incur DO depletion in the test bottle. Any disturbance, whether it is natural or otherwise, to microbial growth, will disrupt the first-order reaction kinetics and hence affect the BOD results [4].

Problem Statement

The presence of reagents such as chlorine (Cl_2), widely used as a disinfectant, in water and wastewater treatment plants in many developing countries, is a good example of the disturbances discussed above. Chlorine is effective in removing coliform organisms such as *Escherichia coli (E. coli)* and *Enterococcus spp.*, by incurring osmotic cellular protoplasmic decomposition [5]. The effects of these types of disinfectants on microbes are widely recognized, though little is known on the implications towards the BOD test itself, when samples due for testing contain elevated levels of the constituent. A chlorine check is typically recommended prior to commencement of BOD_5 analysis [3].

Another perspective is, to look at this in terms of application of the BOD test for assessment of ambient water quality, particularly at the estuarine zone where salinity levels, as a result of chloride (NaCl) is predominant. It has been long accepted that BOD, as a parameter of assessment for organic contamination under such conditions is not preferable, where Total Organic Carbon (TOC) analysis is more preferred [6]. To what extent the chloride content affects the BOD test under brackish conditions, remains ambiguous. TOC analysis though providing a viable, more representative alternative is not necessarily a cost-effective solution, due to limited facilities and equipment [7]. This is even more so true when a comprehensive monitoring network is already in place. It is on this basis that the extent of chloride influences on the BOD_5 test, or more specifically the reaction kinetics involved needs to be further scrutinized.

Methodology

Prior to conducting the analysis, suitable locations for grab sample collection were identified. Since the BOD_5 test is a bio-assay procedure, where the sensitivity of the analysis is directly related to the DO margin between the first and fifth day, it was therefore necessary, to choose locations where organic contamination was known to be significant; in order to encapsulate the maximum degradation, and hence view clear and distinct variations between runs. This was done qualitatively, by correlation to specific land uses. Rivers and streams in the state of Selangor, Peninsular Malaysia that receive significant amount of organic contributions, such as from sullage or greywater, sewage and industrial sources were the best candidates to collect the grab samples. Based on historical monitoring data, these stations were also known to exhibit significant BOD. Five sampling stations were identified; Sg. Rawang (Rawang

river), Sg. Serendah (Serendah river), Sg. Klang (Klang river) and Sg. Damansara (Damansara river, 2 stations, upstream and downstream). The geographical coordinates of these stations are shown in Table 1 below:

Table 1: Location of Sampling Stations

River	Basin	Description	Latitude (N)	Longitude (E)	Station ID
Sg. Rawang	Sg. Selangor	Predominantly receives sewerage pollution input from Rawang town, a tributary of Sg. Serendah.	3° 19'00''	101° 4'00''	S1
Sg. Serendah	Sg. Selangor	Identified as most polluting tributary within Sg. Selangor particularly for organic contaminants such as BOD, COD and NH_3-N	3° 21'00''	101° 33'00''	S2
Sg. Klang	Sg. Klang	Receives input from various types of pollution sources in Selangor state, border transcends to Kuala Lumpur.	3° 2'50"	101° 30'43"	S3
Sg. Damansara (Upstream)	Sg. Klang	A tributary of Sg. Klang, station is prior to receiving industrial effluent from Shah Alam industrial zone, located near TTDI Jaya.	3° 4'25''	101° 33'16"	S4
Sg. Damansara (Downstream)	Sg. Klang	Station located after industrial zone input, but prior to Sg. Klang confluence. Receives treated leachate discharge from Waste Transfer Station.	3° 3'17"	101° 32'56"	S5

All samples collected were incubated at 4°C for about 2 hours, during transit from site to the laboratory. The actual BOD_5 analysis was conducted in accordance with *the American Public Health Association (APHA) Standard Methods for the Examination of Water and Wastewater, Method 5210B.*

Prior to incubation and analysis, sodium chloride (NaCl) solutions were prepared and mixed with the dilution water. This was done with by using gravimetric method, factoring in the solubility limit of the constituent in a 300 ml BOD_5 test bottle under varying salinity levels from 5 parts per thousand (ppt) to 25 ppt for each of the sample collected, at different dilutions. Table 2 below illustrates the amount of NaCl addition required to the achieve the desired salinity ;

Table 2: Amount of Sodium Chloride (NaCl) added to 300ml BOD_5 Test Bottle

Desired Salinity (ppt)	NaCl addition (g)
5	1.5
10	3.0
15	4.5
20	6.0
25	7.5

Lide [10], showed that the solubility of NaCl, at an incubation temperature of 20°C, based on the above desired salinity levels should be close to 100%. DO levels in each of the BOD bottles were monitored daily, to view any variation in decay rate, k_1 and daily BOD. There are many proposed methodologies pertaining to k_1 determination, the one employed in this study is the Thomas' graphical method [8]. This method relies on the following BOD rate equation:

$$BOD_t = L_0(kt)\left[1 + (1/6)kt\right]^{-3} \tag{2}$$

Rearranging this equation, and taking the cube root of both sides yields ;

$$\left(\frac{t}{BOD_t}\right)^{1/3} = \frac{1}{(kL_0)^{1/3}} + \frac{(k)^{2/3}}{6(L_0)^{1/3}}(t) \tag{3}$$

A plot of $(t/BOD_t)^{1/3}$ over time is linear. The intercept and slope are defined as:

$$A = (kL_0)^{-1/3} \tag{4}$$

$$B = \frac{(k)^{2/3}}{6(L_0)^{1/3}} \tag{5}$$

Finally solving for $L_0^{1/3}$, in Eq. 3.11 by substitution of Eq. 3.12 yields:

$$k = 6\left(\frac{B}{A}\right) \tag{6}$$

To summarize, in calculating the bottle decay rate, k or k_1, $(t/BOD_t)^{1/3}$ versus time is plotted on an arithmetic graph and a best-fit straight line is drawn, after which the intercept (A) and slope (B) from the plot is determined and finally k, is calculated based on Eq. 6.

Results and Discussion

Referring to Figure 1 below, unsurprisingly, there is a noticeable difference for the BOD samples tested with varying degrees of salinity. Generally, the bottle decay rate, k_1, decreases as salinity increases, which in turn is an indicator that the chloride is disrupting microbial activity. This hypothesis has been previously established, what is interesting though, is the extent of the effect on the samples tested. After the fifth day, the margin, for Sg. Damansara (downstream) and Sg. Klang samples, exhibited the maximum observable deficiency in BOD (ΔBOD), between lowest and highest salinity at 8 mg/l each (Sg. Damansara (downstream) ; 0 ppt BOD_5 = 15 mg/l, 25 ppt BOD_5 = 7 mg/l; Sg. Klang; 0 ppt BOD_5 = 16 mg/l, 25 ppt BOD_5 = 8 mg/l), a reduction of more than 50%. The lowest variation was in the Sg. Serendah sample at about 1.5 mg/l (25%) which can be considered negligible as the standard error for the BOD test is about 2 mg/l [3].

It should be noted that not all of samples followed the same inverted BOD-salinity relationship. There were also some discrepancies, where higher salinity levels, actually incurred higher BOD (particularly for Sg. Rawang). This phenomenon relates back to the fact that the BOD test is a bioassay procedure, and heterogeneous distribution of organics and microbial populous, may be the root cause. Further observations are required to determine the root cause of the anomaly.

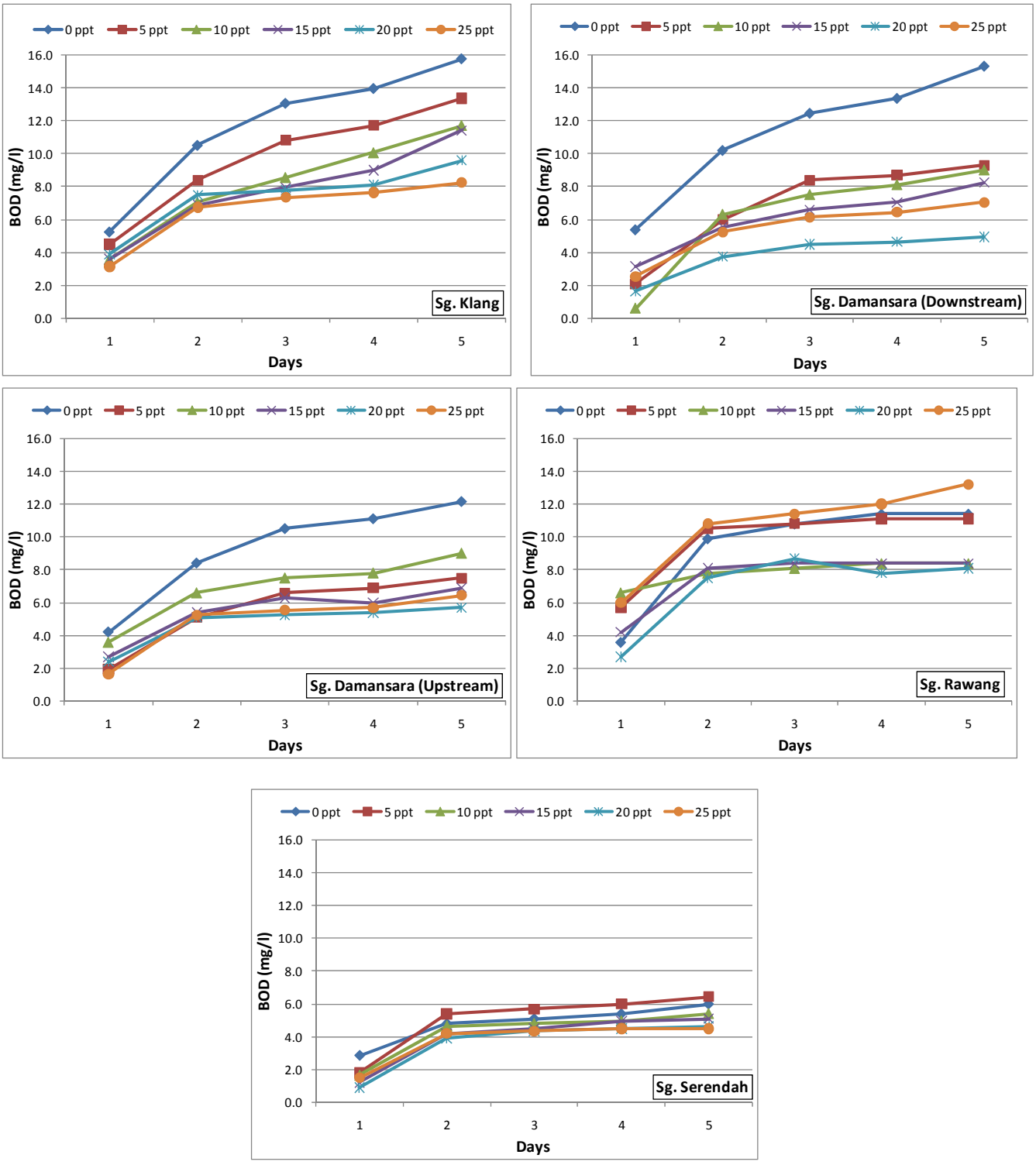

Figure 1: BOD_5 Analysis Results for Varying Induced Salinity Levels

The decay rate analysis, k_1, in accordance with the Thomas graphical method was then conducted, the results of which are summarized in Table 3 and illustrated in Figure 2:

Table 3: BOD Decay Rate, k_1, Analysis Summary

	BOD Decay Rate, k_1 (1/day)				
Salinity (ppt)	**Sg. Rawang**	**Sg. Serendah**	**Sg. Klang**	**Sg. Damansara (Upstream)**	**Sg. Damansara (Downstream)**
0	0.754	0.798	0.306	0.466	0.420
5	0.719	0.663	0.299	0.444	0.390
10	0.691	0.533	0.265	0.416	0.390
15	0.670	0.662	0.257	0.401	0.383
20	0.577	0.626	0.260	0.440	0.251
25	0.513	0.626	0.265	0.243	0.234
Δk_1 ($k_{25ppm} - k_{0ppm}$)	0.241	0.172	0.041	0.223	0.186
$\%\Delta k_1/k_{1(s=0)}$	31.96%	21.55%	13.39%	47.85%	44.29%

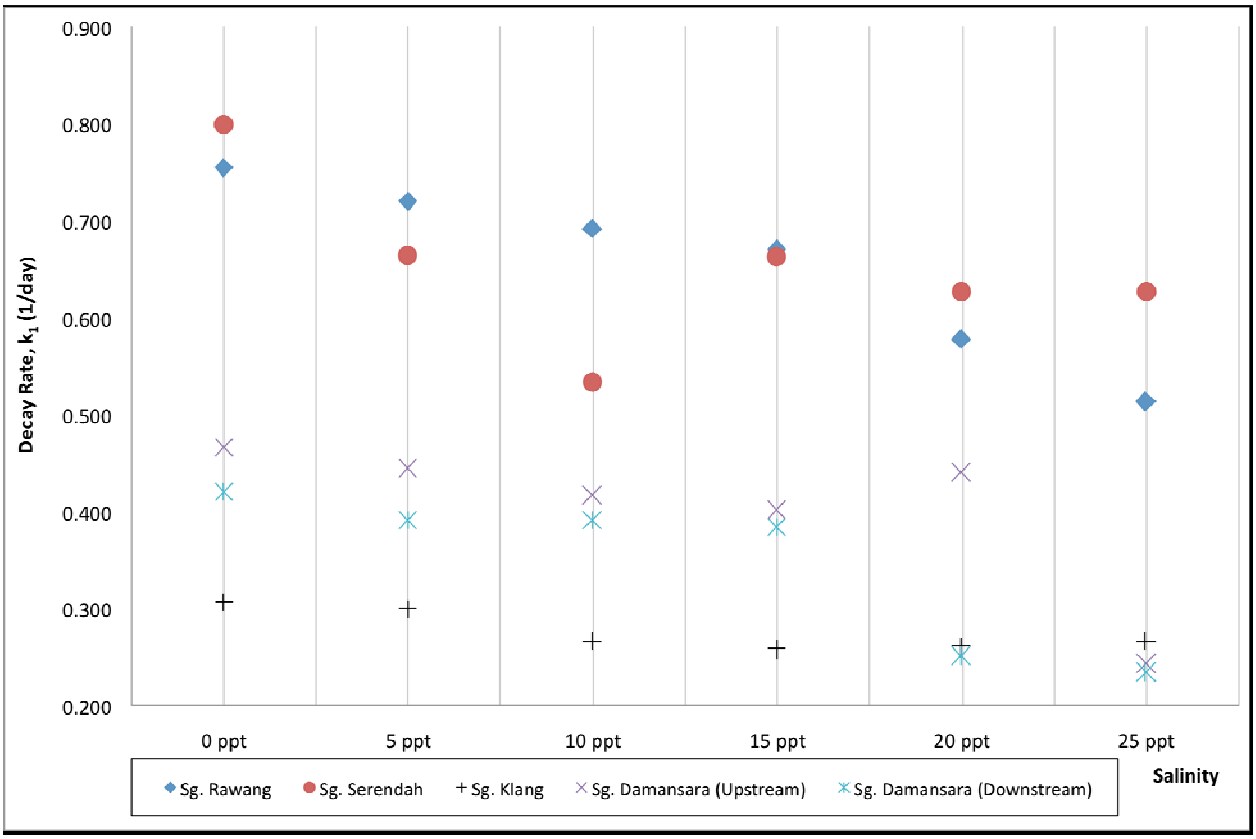

Figure 2: BOD Decay Rate, k_1, Graphical Analysis

Again, it is apparent there is a decrement in the bottle decay rate, k_1, with regards to increasing salinity. The highest quantum was observed in Sg. Rawang at 0.241/day, followed by Sg. Damansara (upstream) at 0.223/day, whereas the lowest quantum was observed at Sg. Klang at 0.041/day. At first glance, this may seem anomalous, because, as mentioned previously, Sg. Klang and Sg. Damansara (downstream) exhibited the highest reduction in terms of overall BOD in the analytical proceedings. What needs to be understood here is that although there seems to be a significant reduction in k_1, (denoted as Δk_1), the influence on the overall in-stream BOD magnitude, still remains relative to the overall/original decay rate, *vis-à-vis*, the ratio $\Delta k_1/k_{1(s=0)}$ is a more indicative contributor of the influence of chloride towards overall BOD reduction. Sg. Rawang for example, though exhibiting a Δk_1 of 0.241/day, only has a relative reduction or $\Delta k_1/k_{1(s=0)}$ of 32% whereas Sg. Damansara (downstream) on the other hand exhibited a $\Delta k_1/k_{1(s=0)}$ of about 44%, an even more significant reduction than the former.

The rate of decrement itself (Δk_1), varies from one sample to the next, which again may be attributed to the mix of microbial populations already present in the sample, as well as the composition and biodegradability of the organic constituents present, which more likely than not, is site specific and relative to input sources. However, it is clear, for there to be any significant reduction in oxygen demand exerted by microbial organisms when stabilizing biodegradable organic matter by salinity/chloride, the margin of relative reduction to the original decay rate ($\Delta k_1/k_{1(s=0)}$) must be significant, whereas the magnitude of reduction (Δk_1) alone is insufficient.

The decay rate in the bottle, k_1 is often misinterpreted as k_d, which is the in-stream decay rate. k_d can differ to k_1 by as much as ten times [8], due to the unrestricted supply of oxygen transfer, occurring at the air-water interface, attributed to re-aeration as well as photosynthesis. Therefore it would also be safe to assume that the decay rate ratio affecting the bottle decay also applies under these conditions as well. The only unaccounted factor relating to BOD kinetics under estuarine conditions is therefore tidal dilution of organic contaminants, which of course has a substantial effect [9]. Albeit being the case, this case study has clearly shown that BOD is not a suitable parameter for assessment of saline waters; the bio-kinetics is simply skewed, as elaborated above.

Conclusion

From the preliminary study conducted above, there is a significant drop in BOD as a result of increasing salinity in all the river water samples collected. This was directly attributed to the influence of chloride in relation to microbial cellular decomposition. Although the magnitude of Δk_1 varies from one sample to the next, the end results subject BOD to further scrutiny as a suitable water quality parameter for monitoring of estuarine zones. In consequence of this observation, other water quality applications which cannot avoid using BOD as an indicator for organic matter, such as in water quality modeling, need to account for the effects of salinity towards microbial activity [6]. A reasonable approximation pertaining to the reduction in decay rate, in particular for tropical rivers can be done using the above results.

References

1. Zainudin, Z. (2008). “The Many Intricacies of Biochemical Oxygen Demand (BOD)”, Institution of Engineers Malaysia (IEM), Featured Article, Jurutera Monthly Bulletin, ISSN 0126-9909, KPDN PP 1050/09/2008 (010721), November 2008.
2. Sawyer, C. N., McCarty, P. L. and Parkin G. F. (2003). “Chemistry for Environmental Engineering and Science : Fifth Edition”. In : Biochemical Oxygen Demand. McGraw-Hill Professional., USA.
3. American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), 2005. “Standard Methods For The Examination of Water and Wastewater : 21st Edition”, APHA, AWWA and WEF.
4. Rasmussen, P. P. and Ziegler, A. C., (2003). “Comparison and Continuous Estimates of Fecal Coliform and Escherichia Coli Bacteria in Selected Kansas Streams”. United States Geographical Survey (USGS).
5. Metcalf and Eddy, Inc. (2004), Revised by: Tchobanoglous, G., Burton, F. L. and Stensel, H. D. “Wastewater Engineering : Treatment and Reuse, Fourth Edition”, McGraw-Hill.
6. Zainudin, Z., Mazlan N. F. and Abdullah, N. (2008). "Low Flow Integration Effects on Water Quality Modeling of Sg. Selangor River Basin with Emphasis on Sewage Pollution Sources”, International Conference and Expo on Environmental Management and Technologies (ICEEMAT’08), Putra World Trade Center (PWTC), December 2008.

7. Baginda, A. R. A. and Zainudin, Z (2009). "Keynote Paper : Moving Towards Integrated River Basin Management (IRBM) in Malaysia", Institution of Engineers Malaysia (IEM), Proceedings, 11th Annual IEM Water Resources Colloquium, ISBN 978-967-5048-46-3.
8. Davis, M. L. and Cornwell, D. A. (1998). "Introduction to Environment Engineering : 3rd Edition", McGraw Hill.
9. Mills, W. B., Bowie, G. L., Grieb, T. M., Johnson, K. M. and Whittemore, R. C. (1986). "Handbook : Stream Sampling for Waste Load Allocation Applications". United States Environmental Protection Agency (US EPA), Washington D. C., USA.
10. Lide, D. R. (2008). "CRC Handbook of Chemistry and Physics, 89th Edition", CRC Press/Taylor and Francis, Boca Raton, FL.